

lowest-energy equatorial orientation. The conformation of the macrocycle is entirely similar to that found for the *trans*-Cr(OCONH<sub>2</sub>)<sub>2</sub>(cyclam) cation (cyclam is 1,4,8,11-tetraazacyclotetradecane) (Bang & Mønsted, 1982).

All bond lengths and angles within the cation are normal for such compounds (Bang & Mønsted, 1982) with Cr–N(mean), Cr–Cl and Cr–O distances of 2.083, 2.307 and 2.090 Å, respectively.

*Acta Cryst.* (1984). **C40**, 1791–1793

## Structure of Bis( $\eta^5$ -trimethylsilylcyclopentadienyl)titanium(IV) Pentasulfide, [Ti(C<sub>5</sub>H<sub>13</sub>Si)<sub>2</sub>]S<sub>5</sub>

BY NIKOLAOS KLOURAS AND STAVROS VOLIOTIS

*Department of Chemistry, University of Patras, Patras, Greece*

AND GABRIEL GERMAIN

*Laboratoire de Chimie Quantique, Université de Louvain, 1348 Louvain-la-Neuve, Belgium*

(Received 13 June 1983; accepted 16 May 1984)

**Abstract.**  $M_r = 482.78$ , monoclinic,  $P2_1/c$ ,  $a = 7.884$  (5),  $b = 14.018$  (14),  $c = 22.352$  (24) Å,  $\beta = 96.28$  (7)°,  $Z = 4$ ,  $V = 2455.4$  (39) Å<sup>3</sup>,  $D_x = 1.30$  g cm<sup>-3</sup>,  $F(000) = 1008$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 8.44$  cm<sup>-1</sup>, room temperature,  $R = 0.10$  for 2382 reflexions. The six-membered heterocycle TiS<sub>5</sub> has a chair conformation. The Ti atom has an irregular tetrahedral environment comprising the bidentate pentasulfide fragment [Ti–S = 2.416 (5) and 2.450 (5) Å] and the two centroids (*R*'s) of the substituted cyclopentadienyl rings (Ti–*R* = 2.076 and 2.059 Å).

**Introduction.** The comparison of the structure of Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub> with that of Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> demonstrates that the substitution of the H atom by a CH<sub>3</sub> group on each cyclopentadienyl ring has a negligible effect on the basic molecular configuration. Specifically, the corresponding bond distances and angles differ by less than 0.01 Å and 1.3°, respectively (Petersen & Dahl, 1975). Moreover, the two cyclopentadienyl rings are symmetrically disposed with respect to the TiS<sub>2</sub> fragment in Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>: The TiS<sub>2</sub> plane approximately bisects the *R*–Ti–*R* angle (Epstein, Bernal & Köpf, 1971; Muller, Petersen & Dahl, 1976). In contrast, no symmetrical positioning of the Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> fragment relative to TiS<sub>2</sub> (which is part of the TiS<sub>5</sub> ring) has been observed in Ti( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>S<sub>5</sub> (II). The normal to the TiS<sub>5</sub> plane forms angles of 32 and 17° with the Ti–*R* ring vectors.

### References

- BANG, E. & MØNSTED, O. (1982). *Acta Chem. Scand. Ser. A*, **36**, 353–359.  
 HOUSE, D. A., HAY, R. W. & AKBAR ALI, M. (1983). *Inorg. Chim. Acta*, **72**, 239–245.  
 HOUSE, D. A. & YANG, D. (1982). *Inorg. Chim. Acta Lett.* **64**, L167–L169.  
 JURNAK, F. A. & RAYMOND, K. N. (1972). *Inorg. Chem.* **11**, 3149.  
 SHELDRIK, G. M. (1981). *SHELXTL User Manual*, 3rd revision. Nicolet XRD Corporation, Cupertino, California.

The purpose of the present work is to elucidate the disposition of the two substituted cyclopentadienyl rings relative to the six-membered TiS<sub>5</sub> ring system in the title compound (I).

**Experimental.** The title compound was prepared by the reaction of Ti[ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> (Köpf & Klouras, 1982) with excess (NH<sub>4</sub>)<sub>2</sub>S<sub>5</sub> in methanol, using a method similar to that described by Köpf & Block (1969) and Köpf & Kahl (1974). After recrystallization from CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1), dark-red glistening crystals were obtained. The compound is air-stable, m.p. 382 K. Composition: found: C = 39.72, H = 5.31 wt% [ $M_r = 482$  (mass spectrum)]; calculated: C = 38.80, H = 5.43 wt%. <sup>1</sup>H NMR peaks were found at  $\tau$ (p.p.m.) 3.97 (*m*) and 4.17 (*m*) (C<sub>5</sub>H<sub>4</sub>, relative intensity 4), 9.77 (*s*) and 9.84 (*s*) [Si(CH<sub>3</sub>)<sub>3</sub>, relative intensity 9].

Syntex diffractometer,  $2\theta$  range 0–47°, graphite-monochromatized Mo *K* $\alpha$  radiation. 3807 reflections measured; after averaging, 2382 independent observed reflections [ $I > 2.5\sigma(I)$ ] remained. Intensities not corrected for absorption or extinction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and refined by blocked full-matrix least squares using *SHELX* (Sheldrick, 1976); all atoms except H considered to be anisotropic. All H atoms placed in geometrically calculated positions. Refinement converged with unit weights to  $R = 0.1034$ .

**Discussion.** The structure of the compound with the atomic numbering is shown in Fig. 1. The positional parameters and the equivalent values of the anisotropic temperature factors for the heavy atoms are given in Table 1.\* Important bond lengths and angles are illustrated in Table 2.

A similar unsymmetrical disposition of the Ti( $\eta^5$ -C<sub>8</sub>H<sub>13</sub>) moiety relative to the TiS<sub>2</sub> plane of the TiS<sub>5</sub> ring, reported for (II), has been observed in compound (I) for the two substituted cyclopentadienyl rings. The corresponding angles are found to be 31.5 and 17.6°.

The values of the S—S distances within the S<sub>5</sub> moiety, and the bond angles as well as the dihedral angles in the six-membered ring are very similar to those found for (II). This comparison indicates that the TiS<sub>5</sub> ring has the same cyclohexane-like chair configuration.

The substituted cyclopentadienyl rings have planar geometry. The differences in C—C bond lengths and angles are not significant.

A comparison of the X-ray structural results for compounds (I) and (II) demonstrates that the substitution of H by the trimethylsilyl group on each cyclopentadienyl ring causes several effects on the basic molecular configuration. The distortion of the tetrahedral coordination about the Ti atom, indicated by the two angles R—Ti—R and S<sub>2</sub>—Ti—S<sub>6</sub>, is greater than that reported for (II). The angles observed are found to be 131.0 and 93.4 (2)°, respectively. The Ti—R distances (2.059 and 2.076 Å) are similar to those in (II). The difference in the average distance of the Ti—S bond length between (I) and (II) is not significant. The Ti—C(cyclopentadienyl) distances are similar to those found in other analogous Ti compounds; the Ti—CSiMe<sub>3</sub> distance is the longest.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles, and angles between normals to planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39461 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

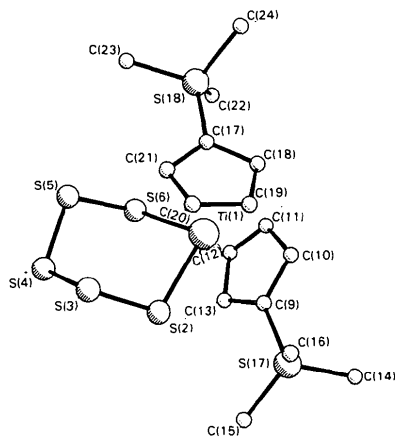


Fig. 1. The molecular structure with the atomic numbering.

Table 1. Atomic positional parameters ( $\times 10^4$ ) and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Ti(1)	828 (3)	5400 (2)	-2692 (1)	2.73
S(2)	1517 (5)	4710 (3)	-3626 (2)	3.99
S(3)	4030 (5)	4331 (3)	-3533 (2)	5.12
S(4)	4104 (6)	3118 (3)	-3025 (3)	5.67
S(5)	4042 (5)	3578 (3)	-2157 (2)	4.95
S(6)	1500 (5)	3933 (3)	-2119 (2)	4.01
Si(7)	-2168 (6)	6007 (4)	-4171 (2)	4.69
Si(8)	2665 (10)	6040 (5)	-1053 (3)	8.46
C(9)	-1798 (16)	5617 (12)	-3355 (7)	3.96
C(10)	-1857 (19)	6212 (12)	-2851 (7)	3.85
C(11)	-1814 (20)	5664 (14)	-2335 (9)	5.57
C(12)	-1866 (19)	4702 (14)	-2494 (8)	4.85
C(13)	-1755 (17)	4649 (12)	-3133 (7)	3.72
C(14)	-4233 (21)	6652 (16)	-4252 (8)	5.98
C(15)	-2315 (24)	4967 (15)	-4677 (8)	6.13
C(16)	-456 (22)	6847 (16)	-4347 (8)	6.33
C(17)	2465 (22)	6245 (12)	-1891 (8)	4.47
C(18)	1371 (24)	6895 (12)	-2195 (8)	4.80
C(19)	1812 (21)	6982 (11)	-2782 (8)	4.59
C(20)	3220 (21)	6379 (12)	-2836 (8)	4.45
C(21)	3564 (18)	5907 (12)	-2316 (8)	4.30
C(22)	879 (52)	5471 (27)	-795 (12)	18.90
C(23)	4687 (44)	5394 (36)	-840 (13)	23.39
C(24)	2976 (49)	7189 (24)	-682 (11)	15.84

Table 2. Important interatomic distances (Å) and angles (°)

R(1) is the centroid of ring 1, R(2) of ring 2.

Ti(1)—S(6)	2.416 (5)	S(2)—Ti(1)—S(6)	93.4 (2)
Ti(1)—S(6)	2.450 (5)	R(1)—Ti(1)—R(2)	131.0
Ti(1)—R(1)	2.076	R(1)—Ti(1)—S(2)	100.2
Ti(1)—R(2)	2.059	R(1)—Ti(1)—S(6)	102.6
		R(2)—Ti(1)—S(2)	111.7
		R(2)—Ti(1)—S(6)	111.1
Ti(1)—C(9)	2.429 (14)	Ti(1)—S(2)—S(3)	108.9 (2)
Ti(1)—C(10)	2.395 (15)	Ti(1)—S(6)—S(5)	109.6 (2)
Ti(1)—C(11)	2.339 (15)	S(2)—S(3)—S(4)	104.0 (3)
Ti(1)—C(12)	2.423 (15)	S(6)—S(5)—S(4)	103.7 (3)
Ti(1)—C(13)	2.406 (14)	S(3)—S(4)—S(5)	105.2 (3)
Si(7)—C(9)	1.895 (17)	C(13)—C(9)—C(10)	106.5 (1.4)
Si(7)—C(14)	1.853 (17)	C(9)—C(10)—C(11)	109.7 (1.5)
Si(7)—C(15)	1.841 (20)	C(10)—C(11)—C(12)	109.2 (1.8)
Si(7)—C(16)	1.865 (18)	C(11)—C(12)—C(13)	107.3 (1.6)
C(9)—C(10)	1.408 (20)	C(12)—C(13)—C(9)	106.9 (1.5)
C(10)—C(11)	1.382 (22)	C(14)—Si(7)—C(9)	106.0 (7)
C(11)—C(12)	1.394 (25)	C(15)—Si(7)—C(9)	110.8 (8)
C(12)—C(13)	1.443 (22)	C(15)—Si(7)—C(14)	109.3 (9)
C(13)—C(9)	1.444 (22)	C(16)—Si(7)—C(9)	110.3 (7)
S(2)—S(3)	2.040 (5)	C(16)—Si(7)—C(14)	108.7 (1.0)
S(3)—S(4)	2.043 (7)	C(16)—Si(7)—C(15)	111.6 (9)
S(4)—S(5)	2.051 (8)		
S(5)—S(6)	2.076 (6)		

The disposition of the two cyclopentadienyl rings makes the ten ring protons of (II) magnetically nonequivalent. In solution this is manifested by the detection of two sharp NMR peaks at room temperature (Köpf, Block & Schmidt, 1968). In our compound this effect influences not only the eight cyclopentadienyl protons (two multiplets due to the coupling), but also the NMR peaks of the two Si(CH<sub>3</sub>)<sub>3</sub>

groups (two singlets).  $\{Ti[C_5H_4Si(CH_3)_3]_2Cl_2\}$  shows only one singlet for the 18 methyl protons (Köpf & Klouras, 1982.)

We are grateful to Mrs Alice Stöckel, Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, for recording the mass spectra.

#### References

- EPSTEIN, E., BERNAL, J. & KÖPF, H. (1971). *J. Organomet. Chem.* **26**, 229–245.  
 KÖPF, H. & BLOCK, B. (1969). *Chem. Ber.* **102**, 1504–1508.  
 KÖPF, H., BLOCK, B. & SCHMIDT, M. (1968). *Chem. Ber.* **101**, 272–276.  
 KÖPF, H. & KAHL, W. (1974). *J. Organomet. Chem.* **64**, C37–C41.  
 KÖPF, H. & KLOURAS, N. (1982). *Chem. Scr.* **19**, 122–123.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MULLER, E., PETERSEN, J. & DAHL, L. (1976). *J. Organomet. Chem.* **111**, 91–112.  
 PETERSEN, J. & DAHL, L. (1975). *J. Am. Chem. Soc.* **97**, 6422–6432.  
 SHELDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1984). **C40**, 1793–1795

### 3,3-Di-*tert*-butyl-*N*,4,5,6,7-pentaphenyl-1,2-dihydro-1,2,3-diazastannepine-1,2-dicarboximide Monohydrate, $C_{44}H_{43}N_3O_2Sn \cdot H_2O$

BY HANS PREUT, RAINER MARX AND WILHELM PAUL NEUMANN

*Abteilung Chemie der Universität Dortmund, Postfach 500500, D-4600 Dortmund 50, Federal Republic of Germany*

(Received 4 April 1984; accepted 12 June 1984)

**Abstract.**  $M_r = 782.6$ , monoclinic,  $C2/c$ ,  $a = 22.838$  (7),  $b = 14.526$  (5),  $c = 26.270$  (9) Å,  $\beta = 115.32$  (5)°,  $U = 7878$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.320$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 0.70$  mm<sup>-1</sup>,  $F(000) = 3232$ ,  $T = 294$  (1) K. Final  $R = 0.057$  for 2500 unique observed diffractometer data. The central part of the asymmetric monomeric molecule is a seven-membered heterocycle consisting of a tetrahedrally coordinated Sn, two N and four C atoms. Two *tert*-butyl groups and four phenyl groups are bound to this ring. The two N atoms are part of an annellated *N*-phenylurazole ring.

**Introduction.** The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the 1:1 adduct of 1,1-di-*tert*-butyl-2,3,4,5-tetraphenyl-1-stanna-2,4-cyclopentadiene with 4-phenyl-3,4-dihydro-1,2,4-triazole-3,5-dione indicated a 7-stanna-8,9,10-trinorbornene structure because of the existence of two non-equivalent *tert*-butyl groups. The high stability of the title compound (m.p. 498 K without decomposition), however, could not be explained in comparison with similar compounds such as the dimethyl- and diisopropylstanna analogues which decompose instantaneously with the elimination of the dialkylstannylene. Only the stanna-8,9,10-trinorbornene resulting from tetracyanoethylene and the 1,1-dimethyl-2,3,4,5-tetraphenylstannole can be isolated at 243 K (Grugel, Neumann & Schriewer, 1979). IR and mass spectrometry did not give clear information about the structure of the title compound.

Therefore an X-ray structure analysis has been undertaken.

**Experimental.** Colourless crystals obtained by recrystallization from methylene chloride/diethyl ether;  $\omega/2\theta$  scan, scan speed 0.83–5° min<sup>-1</sup> in  $\theta$ , Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$ , crystal 0.12 × 0.20 × 0.30 mm, lattice parameters from least-squares fit with 25 reflexions in the range  $6.9 \leq \theta \leq 12.1^\circ$ ; three standard reflexions recorded every 3 h showed no decrease; 4027 reflexions measured,  $2 \leq \theta \leq 20^\circ$ ,  $h - 22 \rightarrow +22$ ,  $k 0 \rightarrow +14$ ,  $l 0 \rightarrow +25$ ; Lorentz–polarization and absorption correction *via*  $\psi$  scans, max./min. transmission 1.00/0.96; systematic absences ( $hkl$ )  $h+k = 2n+1$ , ( $h0l$ )  $l = 2n+1$ , possible space groups  $C2/c$  and  $Cc$ ; structure solution in space group  $C2/c$  *via* Patterson function,  $\Delta F$  syntheses and full-matrix least squares with 2500 observed reflexions [ $|F_o| > 3\sigma(F_o)$ ], anisotropic temperature factor for Sn and isotropic for O, N, C, H; H atoms placed in geometrically calculated positions (C–H 0.95 Å) before last refinement cycles, not refined ( $B = 5.0$  Å<sup>2</sup>); a  $\Delta F$  synthesis with all non-H atoms of the molecule revealed two peaks which were interpreted as a split O atom of a water molecule [occupancy factor for O(3) 0.67 and for O(4) 0.33]; complex neutral-atom scattering factors from Cromer & Waber (1974) and Cromer (1974) (H: SDS, C: RHF), least-squares